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A MEASUREMENT OF THE HYDROGEN YIELD
IN THE RADIOLYSIS OF WATER
BY DISSOLVED FISSION PRODUCTS

by

M. C. Sauer, Jr., E. J. Hart,
K. F. Flynn, and J. E. Gindler

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ABSTRACT

Hydrogen from the radiolysis of water by dissolved fission products is stripped from the solution and collected by bubbling CO_2 through the solution. Quantitative measurements of the G value for hydrogen show that the yield is essentially the same as would be obtained by external gamma radiolysis of nonradioactive solutions of the same chemical composition. The hydrogen yield can be enhanced by addition of a hydrogen-atom donor, such as formic acid, to the solution. The yield of hydrogen from fission-waste solutions is discussed with respect to the question of whether it represents a significant energy source.

I. INTRODUCTION

The question of whether useful amounts of hydrogen can be generated via the radioactive decay of fission-waste products provided the impetus for the experiments described here. Previous radiation chemical studies* of aqueous solutions using external radiation sources, such as ^{60}Co gamma radiation, allow one to calculate the yield of hydrogen expected from solutions of fission-waste products if the assumption is made that energy deposited by the beta and gamma radiation from the fission products has the same efficiency in producing hydrogen as in the case of the ^{60}Co gamma radiolysis. Although this assumption is reasonable, no quantitative measurements had been made on fission-product solutions. The results obtained show that the assumption is valid, and the conclusion is reached that the amount of hydrogen that could be obtained from fission-waste solutions is economically insignificant.

II. EXPERIMENTAL PROCEDURE

A. The Fission-product Solution

A 10-mg sample of uranium (93% ^{235}U) was sealed in a thin-walled quartz bulb (~1/2-in. diameter) under about 0.5 atm helium. This bulb was packed

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*A recent summary of this field is given in Ref. 1.

tightly in aluminum foil in an aluminum can ($3 \times 1\frac{1}{4}$-in. diameter). The lid was beam-welded onto the can under vacuum.

The sample was placed in the CP-5 reactor for one month at 5×10^{13} n cm^{-2} sec^{-1}. The aluminum can was opened 80 days after completion of the irradiation, using a remote-controlled, electrically operated tubing cutter. All operations were performed in a hot-lab cave using hand-operated remote manipulators. The quartz bulb was placed in a 10-ml Pyrex beaker. The bulb was broken by placing a metal pipe on top of the quartz bulb and dropping a metal rod through the pipe, the extent of travel of the rod being limited by a rubber collar on the rod to prevent the rod from contacting the beaker.

One and one-half ml of HNO_3 (12 $\underline{M}$) were added to the sample, and the beaker was covered and allowed to stand overnight. Three ml of H_2O were then added to the beaker to bring the nitric acid concentration to the desired level for the experiments to be described. A radiation monitor was used to determine approximately how much activity dissolved by measuring the activity of the beaker before and after decanting the liquid to the reservoir on the reaction vessel. About 50% of the activity remained in the beaker. An attempt was made to dissolve more activity by adding 2 ml of 16 $\underline{M}$ HNO_3 and allowing the sample to stand for 4 days. Less than 10% of the remaining activity dissolved in the nitric acid. The activity therefore was either in the quartz or from fission products that were not soluble under the conditions used.

B. The Reaction Vessels

The overall experimental operation is indicated in the block diagram shown in Fig. 1. The reaction-vessel section is shown in detail in Fig. 2. The apparatus was constructed from Pyrex except for the valves, which were Kel-F, and the 1/16- and 1/8-in. Teflon tubing used to connect the valves with the Pyrex. (The 1/16-in. tubing was used where minimum liquid volume was desired, i.e., between R and A and between A and B.)
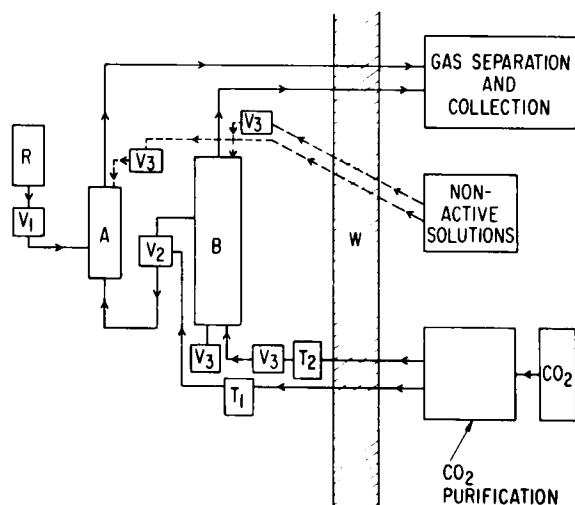

Fig. 1

Block Flow Diagram of Apparatus. R: reservoir for solution of fission products; A: small reaction vessel (0-20 cc); B: large reaction vessel (20-250 cc); V_1-V_3: remote-controlled, air-pressure-operated values from Laboratory Data Control; V_1 is #CAV2031K, V_2 is #CAV3031K (three-way valve), and V_3 is #CAV2060K; T_1 and T_2 "safety" traps; W: shielding wall.
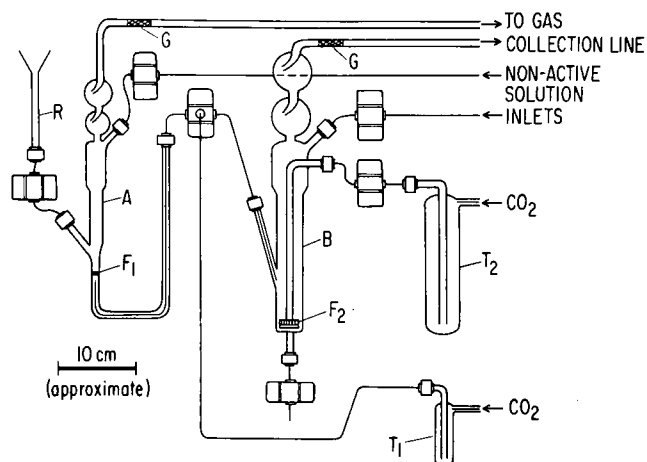
Fig. 2

Reaction–vessel Arrangement. F_1: medium-porosity fritted glass disk; F_2: fine-porosity fritted glass disk; G: Pyrex glass wool (loosely packed). The other symbols are defined in the legend for Fig. 1.

The nitric acid solution of the fission products passed through a sintered glass filter (to remove small particles of quartz) into the reservoir (R). This reservoir, as well as the reaction vessels (A and B), had volume-calibration marks. Part of the solution was allowed to flow from the reservoir to vessel A, while CO_2 was flowing through the fritted glass disk F_1, the pressure in A being about 0.5 atm. The CO_2 bubbled through the solution, carrying with it the H_2 produced by radiolysis, was collected, and the H_2 was separated, as described later. Water was added in increments through the nonactive-solution inlet, and the gas analysis was repeated until the volume in A reached about 20 cc.

Then the contents of A were transferred to B by opening the valve connecting A and B (see Fig. 2) and putting CO_2 pressure (about 1.5 atm) on the liquid in A through the nonactive-solution inlet. During this transfer, CO_2 was flowing through the fritted glass disk F_2, the pressure in B being about 1.5 atm. The CO_2 bubbling through the solution in B was collected and analyzed for H_2, addition of nonactive solutions being made as desired through the nonactive-solution inlet on B. The valve at the bottom of B was used to drain the solution; a measured aliquot was used to determine the activity per unit volume.

The traps T_1 and T_2 had volumes somewhat larger than vessels A and B, respectively, and were present as a safety feature to prevent the radioactive solution from "backing up" (as a result of accidental pressure imbalance) into the CO_2 source. The outlet tubes from tops of A and B were loosely packed with glass wool to decrease the possibility of liquid droplets being carried along by the CO_2 stream.

C. CO_2 Purification and Storage

The source of CO_2 was a tank of Matheson "Coleman"-grade CO_2. The CO_2 entered the apparatus as shown in Fig. 3 and was frozen in the first trap at liquid-nitrogen temperature with a vacuum on the exit side of the trap. The CO_2 was then distilled to the second trap with a vacuum on the exit side. Further trap-to-trap distillations were found to be unnecessary. The CO_2 was

stored in the second trap at -78°C and was allowed to flow to the reaction vessels, when needed, by opening the appropriate stopcocks in Fig. 3 and reaction-vessel valves (see Figs. 1 and 2), as well as the stopcocks and valves shown in Fig. 4.
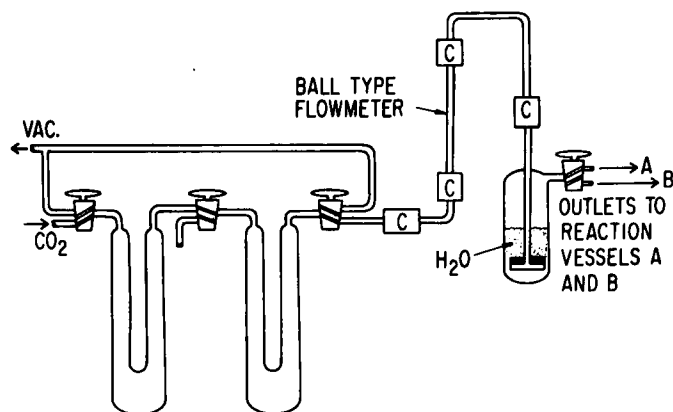
Fig. 3

CO_2 Purification and Storage Apparatus.
C: "Cajon" O-ring fittings for 1/4-in. tubing.

Fig. 4

Gas-collection and -separation Apparatus. S: solenoid; M: iron pipe; Z: solenoid valve; C: check valve, Circle Seal, Model 259B-3PP; R: pressure relief valve; P: pressure sensor; J: ball joints.
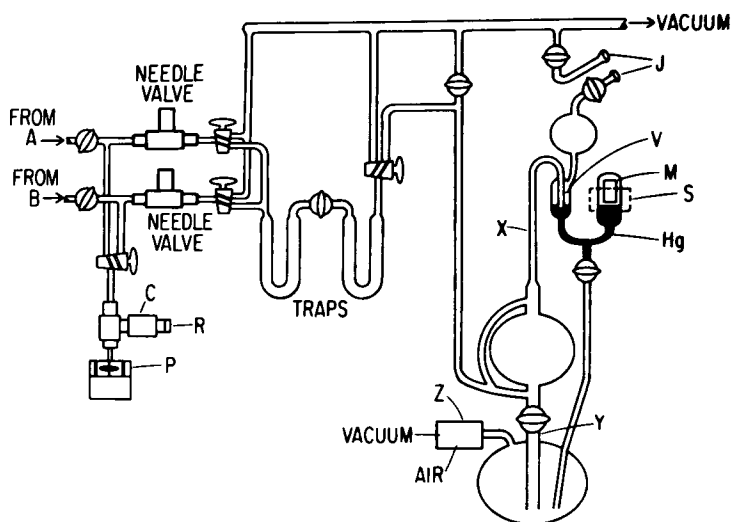
D. Gas-separation and -collection Apparatus

Figure 4 shows the vacuum line used for collection of the CO_2-H_2 mixtures coming from the reaction vessels. The apparatus was evacuated before opening the stopcock to either reaction vessel A or B. The needle valves allowed very fine control of the CO_2 flow rate, which was monitored by the flowmeter in Fig. 3. Also, because the rate of flow of CO_2 through the needle valve should be proportional to the pressure on the upstream side of the needle valve, this pressure was monitored by pressure sensor P (see Fig. 4).

The CO_2 passing through the needle valve was pumped away during the equilibration period (up to 18 hr). Then the appropriate stopcock was turned to allow the CO_2 to flow into the first trap, which was at liquid-nitrogen temperature. The CO_2 was collected for a measured time (1-2 hr), during which the Toepler pump was operating, thereby collecting the hydrogen and other

gases (oxygen and nitrogen) not frozen at liquid-nitrogen temperature. The CO_2 was then distilled to the second trap; this process was sufficient to collect essentially all the gases entrapped in the frozen CO_2.

The Toepler pump system was designed for automatic operation and had a mercury valve, the design of which ensured that the amount of the gas coming through the traps that was not collected was negligible. The mercury valve was adjusted by allowing mercury from the reservoir to fill the two arms as shown in Fig. 4, the system being initially evacuated. The mercury level was such that it just closed off the inlet tube at V. Inductance-type switches were incorporated in an electrical circuit so that, when the mercury level was below point Y, the solenoid valve Z opened to the atmosphere, causing the mercury to rise. When the mercury reached point X, where a second inductance lead was placed, the solenoid S was activated, causing the metal pipe M to be raised. This in turn caused the mercury level to drop sufficiently at V to allow gas to flow into the spherical bulb above V.

The electrical circuit was designed so that a short time after solenoid S was activated, solenoid Z was deactivated, thereby opening the reservoir to vacuum and causing the mercury level to drop before it spilled over into the mercury valve. Each cycle took about 40 sec; on the final cycle, the mercury was allowed (by manual operation) to spill over into the mercury valve and to continue into the spherical bulb, forcing the gas into a U-tube collecting device. This U tube was then removed, and the gas sample was introduced into a gas chromatograph.

The limiting factor in the efficiency of the operation of the valve, except on the last cycle, where the mercury spills over, is the ratio of the small volume of the inlet tube from point V back to the point of maximum travel of the mercury column to the larger volume of the spherical bulb above V. Therefore, the tubing above X had a small inside diameter (about 2 mm).

A safety feature, shown in Fig. 4, is the check valve and relief valve, which were incorporated in the apparatus to prevent the pressure from rising significantly above 1 atm in the event that the temperature of the bath surrounding the CO_2 reservoir accidentally increased.

E. Analysis of Gases

The U-shaped tube used for collecting the gas from the Toepler pump was constructed with two two-way stopcocks so that it could be put on the gas chromatograph and flushed out with carrier gas before turning both stopcocks to introduce the sample. A 12-ft column of molecular sieve 13X was used, which gave more than adequate separation, the retention times being 2, 5, and 13 min for hydrogen, oxygen, and nitrogen, respectively.

The instrumental sensitivity for hydrogen and oxygen was determined by introducing a known quantity of argon containing a known percentage of either hydrogen or oxygen. Argon was used as the carrier gas in the chromatograph.

F. Dosimetry

The rate of energy dissipation in the solution of fission products was determined by evaporating a known volume of the fission-product solution to dryness and adding 100 cc of Fricke dosimeter solution (0.4 $\underline{M}$ H_2SO_4, 10^{-3} $\underline{M}$ $FeSO_4$, and 10^{-3} $\underline{M}$ NaCl). The absorbance (at 304.0 nm) of this solution was then measured, using a 10-cm cell, over a period of about 3 days. The slope of the resulting linear plot of absorbance versus time allowed the dose rate to be calculated directly from the known $G(Fe^{+3})$ value.

In principle, a correction should be made for the different geometries of the 10-cm Cary cell and the reaction vessel in which the hydrogen was generated. However, this correction is estimated to be less than a few percent, so it has been neglected.

III. RESULTS

The radioactivity content of the fission-product solution was found to be insufficient to make measurements of $G(H_2)$ at nitric acid concentrations between 0.5 and 4 $\underline{M}$. Attempts to measure $G(H_2)$ in this concentration range were unsuccessful; i.e., the hydrogen peak obtained by gas chromatography was essentially identical to that obtained by operating the gas-collection apparatus using nonradioactive nitric acid solutions. However, because $G(H_2)$ increases as the HNO_3 concentration is decreased, a measurable yield of hydrogen was obtained when 3.2 ml of the fission-product solution was diluted to 150 ml, making the concentration of HNO_3 0.08 $\underline{M}$. In this case, the observed hydrogen peak was about three times as great as "background." After the background was subtracted, the hydrogen production rate was 0.035 μmoles of hydrogen per hour. The reproducibility was good, four 1-hr runs yielding hydrogen peaks of 17.7, 18.0, 18.1 and 17.9. The "background," as determined earlier, on non-radioactive solutions, was 6 ± 1.

The results of the dosimetry are exemplified in Fig. 5, where the absorbance at 304.0 nm due to Fe^{+3} is seen to increase linearly with time. A small intercept at time zero is observed that is almost certainly due to oxidation of Fe^{+2} by various fission-product metal ions. The slope of the plot shown in Fig. 5 yields directly a dose rate in the dosimeter sample of 50.7 rads/hr. This must be corrected for 13 days of decay to the time at which the hydrogen yields were measured. The corrected value is 59 rads/hr, based on fission-product decay data in Ref. 2. Corrections for aliquot fraction and dilution result in an energy dissipation rate of 1.07×10^{19} eV/hr (1.14×10^3 rads/hr) in the 150 cc of solution from which the hydrogen yield was measured. From this value and the observed hydrogen production rate of 0.035 μmoles/hr, a value of $G(H_2) = 0.197$ is obtained.

In principle, the yield of oxygen could also be measured in these experiments; however, the yield is small and the sensitivity of the gas chromatograph

(with argon carrier gas) for oxygen is about 10 times less than for hydrogen. Furthermore, small amounts of nitrogen and oxygen were always obtained in blank experiments with inactive solutions, apparently due to small leaks as-sociated with the plastic valves. Hence, only the hydrogen yields could be measured.
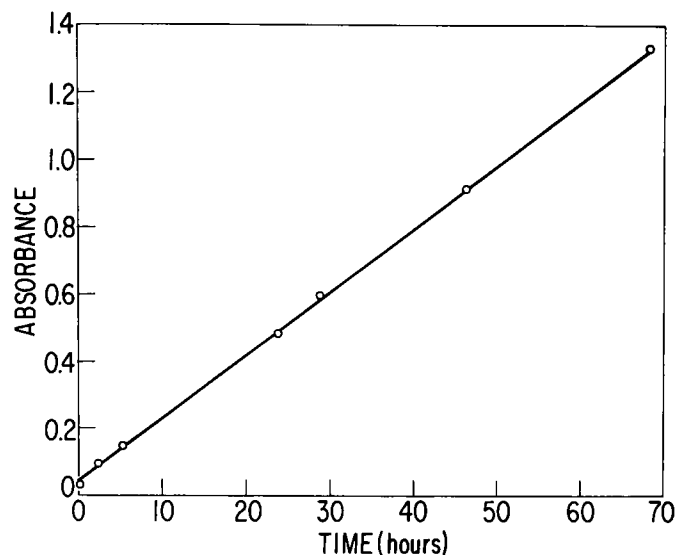

Fig. 5

Fission-product Dosimetry. An aliquot of the fission-product solution was evaporated to dry-ness and dissolved in 100 ml of Fricke dosim-eter solution (0.8 N H_2SO_4, 10^{-3} M Fe^{++}, 10^{-3} M NaCl) at time zero. The absorbance at 304.0 nm is shown as a function of time.

The yield was also determined under conditions in which most of the hydrated electrons were converted to hydrogen atoms, and a hydrogen-atom donor (formic acid) was present from which the hydrogen atoms could abstract hydrogen. The exact conditions were $[NO_3^-]$ = 0.027 $\underline{M}$, $[H^+]$ = 0.29 $\underline{M}$ (by adding sulfuric acid), and [formic acid] = 2.7 $\underline{M}$. Under these conditions the hydrogen evolution rate was considerably enhanced, $G(H_2)$ being 2.4_3.
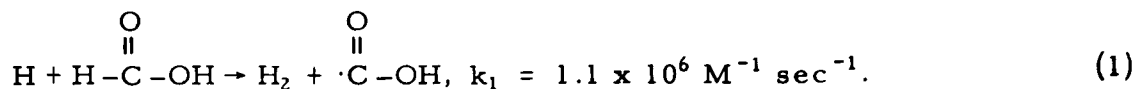

IV. DISCUSSION AND CONCLUSIONS

A. Comparison of Observed and "Expected" $G(H_2)$

The observed yields of hydrogen can be compared with yields calculated on the basis of known reaction-rate constants and the yields of primary species obtained in previous aqueous radiation chemistry studies.

The expected yield of hydrogen at $[H^+]$ = $[NO_3^-]$ = 0.08 $\underline{M}$ can be esti-mated from results on the effect of such reactants on the molecular hydrogen yield.[3] (These results are also discussed on page 77 of Ref. 1.) In pure water, the yield of hydrogen is 0.45 molecules/100 eV, but 0.08 $\underline{M}$ H^+ reduces the yield to 0.32, and 0.08 $\underline{M}$ NO_3^- reduces the yield to 0.25. The combined effect of H^+ and NO_3^- at 0.08 $\underline{M}$ should cause a reduction to about 0.22-0.23, which is near the value of 0.19_7 observed here. Therefore the result obtained in this work can be seen to be sufficiently near the value expected on the basis of previous aqueous radiation-chemistry studies of water to justify the conclusion that the radiolytic action of dissolved fission products is not different from the action of the external radiation sources used in previous studies.

Further support of this conclusion is given by the results of the formic acid experiments. The $G(H_2)$ can be predicted in these experiments from the known primary G values of H_2, H, and e_{aq}^-, and the rate constants for the reactions of these species with H^+, NO_3^-, and formic acid.

The main effect of the addition of formic acid is that hydrogen atoms, which would otherwise react in ways that would not yield hydrogen, will abstract H from formic acid to produce H_2. The main reaction is
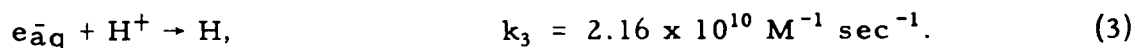
$$H + H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightarrow H_2 + \cdot\overset{\overset{\displaystyle O}{\|}}{C}-OH, \quad k_1 = 1.1 \times 10^6 \text{ M}^{-1}\text{ sec}^{-1}. \tag{1}$$

The fraction of H atoms which yield H_2, f_{H_2}, is determined by the competition between reaction 1 and

$$H + NO_3^- \rightarrow HNO_3^-, \quad k_2 = 2.4 \times 10^7 \text{ M}^{-1}\text{ sec}^{-1}. \tag{2}$$
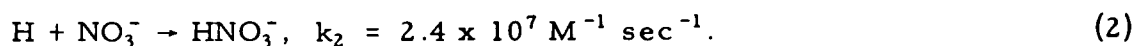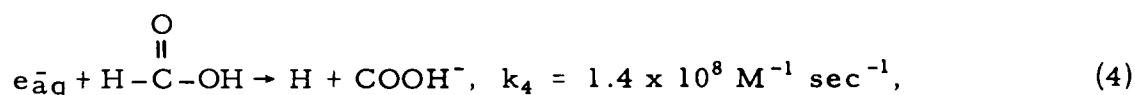
At the concentrations used (see Sec. III above),

$$f_{H_2} = \frac{k_1[\text{HCOOH}]}{k_1[\text{HCOOH}] + k_2[\text{NO}_3^-]} = 0.82.$$

Most of the hydrogen atoms originate from hydrated electrons via the reaction

$$e_{aq}^- + H^+ \rightarrow H, \quad k_3 = 2.16 \times 10^{10} \text{ M}^{-1}\text{ sec}^{-1}. \tag{3}$$

The reactions

$$e_{aq}^- + H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightarrow H + COOH^-, \quad k_4 = 1.4 \times 10^8 \text{ M}^{-1}\text{ sec}^{-1}, \tag{4}$$

and

$$e_{aq}^- + NO_3^- \rightarrow NO_3^=, \quad k_5 = 1.1 \times 10^{10} \text{ M}^{-1}\text{ sec}^{-1}, \tag{5}$$
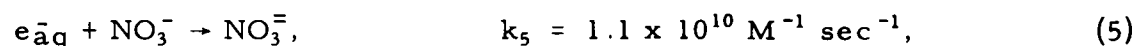
are in competition. The fraction e_{aq}^- converted to H atoms is therefore

$$f_H = \frac{k_3[H^+] + k_4[\text{HCOOH}]}{k_3[H^+] + k_4[\text{HCOOH}] + k_5[\text{NO}_3^-]}$$

or $f_H = 0.96$.

To calculate $G(H_2)$, one must know the three primary G values, which are represented by the designations $g(H)$, $g(e_{aq}^-)$, and $g(H_2)$. In pure water,

g(H) is 0.71 (see page 74 of Ref. 1); considering the combined effects of the H^+, NO_3^-, and formic acid present, this would be lowered to about 0.6. The effect of these components on $g(H_2)$ can likewise be estimated (see page 77 of Ref. 1); $g(H_2)$ in pure water is 0.45, but would be lowered to about 0.3. The primary yield of e_{aq}^- is 2.8. (See page 142 of Ref. 1.) From these values, the predicted yield of H_2, $G(H_2)$, is given by

$$G(H_2) = g(H_2) + f_{H_2}[f_H g(e_{aq}^-) + g(H)]$$

or $G(H_2) = 3.0$.

This calculated $G(H_2)$ is in reasonable agreement with a value of 2.7 obtained (by interpolation) from gamma-radiolysis results of Smithies and Hart[4] on $G(H_2)$ versus [HCOOH] in water. Actually, the latter authors found $G(H_2)$ to decrease from 3.2 at 1 M HCOOH to 2.4 at 5 M HCOOH due to complicating reactions (involving formic acid) not considered above. Therefore, our experimental value of 2.43 shows that there is no large difference in $G(H_2)$ obtained using dissolved fission products as opposed to ^{60}Co gamma radiolysis.

B. Hydrogen Evolution from Processed Fission-waste Solutions

It is of interest to examine this subject from the standpoint that useful quantities of hydrogen may possibly be generated from fission-waste solutions. Indeed, this was an impetus for the experiments described in this report. From the following, one can see that the energy value of the hydrogen generated from fission-waste products would be relatively small.

One can estimate the total quantity of fission-waste products that will be produced from the present to the year 2000 from figures given by Schneider.[5] From this, an order-of-magnitude estimate can be made of the average hydrogen production rate that could be obtained by utilizing the energy liberated via radioactive decay. Based on the primary molecular hydrogen yield of 0.45 molecules/100 eV, we obtain 10 tons per day; addition of a hydrogen-atom donor could increase this about a factor of six.* Hydrogen production rates in this range are not insignificant, but are small compared with the average daily usage (1972) of hydrogen in the U. S. of about 2×10^4 tons. The value of hydrogen is about \$300/ton. It does not seem likely that a safe, efficient process could be designed that would make the collection of the hydrogen produced from fission-waste solutions economically feasible.

In understanding why more significant amounts of hydrogen would not be obtained from the radioactive decay of fission products, we can view the

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*We have shown that the addition of a hydrogen–atom donor such as formic acid enhances the G value for hydrogen to about 2.4 molecules per 100 eV absorbed. For this process to yield a net gain, however, more than one molecule of hydrogen must be produced per molecule of formic acid consumed, because the formic acid has a fuel value of about one molecule of hydrogen. This conclusion results from the fact that the reaction $HCOOH \rightarrow H_2 + CO_2$ has a negative ΔG; i.e., the thermal decomposition of formic acid can be readily catalyzed. Therefore, both of the hydrogen atoms of formic acid would have to be abstracted by radiolytically generated hydrogen atoms to achieve a gain of a factor of 2 in the "energy" yield.

process in terms of the energy release per fission. About 12% of the energy released per fission is stored as nuclear instability of radioactive fission products.[6] (82% of the energy from ^{235}U fission goes into the kinetic energy of the fission fragments, and 6% is accounted for by prompt gamma rays and neutrons emitted within about 1 msec of the fission event.) At first glance, this would seem to be an appreciable source of energy if it could be used to convert water into hydrogen. However, much of the radioactive decay will occur while the reactor is operating; a rough estimate is that 90% of the radioactivity produced would decay before the used fuel is removed. Of the remaining energy stored as radioactivity, a considerable fraction cannot be absorbed by an aqueous solution, i.e., energy carried away by the neutrino in beta decay. If we take a value of 50% for the latter, we have 0.12 x 0.1 x 0.5 = 0.006 as the fraction of the energy produced by fission that can be used to radiolytically decompose water.

Of course, this energy is not used with 100% efficiency in producing hydrogen. If we use 3 eV per molecule as the energy value of hydrogen (i.e., the heat of combustion), and a G value of hydrogen production of 2.5 molecules/100 eV, we see that the radiolytic process is only 7.5% efficient. Therefore, the energy content of the hydrogen produced relative to the energy liberated per fission would be 0.006 x 0.075, or about 0.05%.

It is of interest in regard to the above to consider the efficiency of hydrogen production in the case of a homogeneous reactor, where the kinetic energy of the fission fragments decomposes water with a G value in the range of 1.5-1.8 molecules/100 eV. In this case, the hydrogen energy content would be about 5 eV per 100 eV absorbed, and the overall result would be that 4% of the energy released per fission would be stored in hydrogen (i.e., 80% times 5%). This represents a potentially significant fraction of the energy output of a reactor.

ACKNOWLEDGMENTS

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